## 216. *The System Zinc Sulphate–Ammonia–Water.*

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THE separation of two liquid layers in this system was first observed by André (*Compt. rend.*, 1885, **100**, 241) on passing ammonia gas into a solution of the salt in well-cooled aqueous ammonia. The layers had at 8° the compositions

| | Upper layer. | Lower layer. |
|---|---|---|
| $NH_3$, % | 25·69 | 22·16 |
| Zn, % | 2·15 | 13·62 |
| Density | 0·953 | 1·2714 |

The system evidently differs essentially from the only two carefully investigated ammoniacal systems in which separation of liquids occurs, *viz.*, tribasic potassium phosphate (Jänecke, *Z. physikal. Chem.*, 1927, **127**, 71) and potassium carbonate (Applebey and Leishman, preceding paper). In these systems ammonia is very unequally distributed between the phases, while André's results show only slight difference of ammonia concentration in the two phases.

On passing more ammonia, André noted the formation of small felted needles to which, on analysis of the partially dried solid, he gave the formula $ZnSO_4,2NH_3,3H_2O$. A temperature of 36° was the highest at which André was able to obtain two layers, but as the system was not saturated with solid, the upper critical solution temperature was not given by this observation.

## EXPERIMENTAL.

The methods used were identical with those described in the preceding communication. The system was completely explored at 0° and 18°.

The zinc sulphate used was an A.R. specimen of the heptahydrate. Qualitative analyses showed only traces of magnesium and iron. The salt was always added to the systems under investigation as a saturated solution of the heptahydrate or monohydrate (prepared by dehydration) in concentrated ammonia; in the preparation of these solutions the trace of iron separated and was filtered off.

The equilibrium solutions and wet solids were analysed for ammonia and zinc, the volumetric ferrocyanide method being used in strong solutions, and the gravimetric pyrophosphate method when the solutions were too dilute for accurate volumetric estimation. These methods of analysis, which would not have revealed any occurrence of basic products, were only adopted when the composition of the two liquid layers and wet solid of the four-phase system at 18° had been completely analysed as follows: (*a*) For ammonia: (1) by direct titration (free ammonia); (2) by distillation with excess of alkali (total ammonia). (*b*) For zinc sulphate: (1) as zinc pyrophosphate; (2) as barium sulphate.

The results obtained [which are given as the weights (in g.) in the total sample taken] were:

| | $NH_3$. | | $ZnSO_4$. | |
|---|---|---|---|---|
| | Direct. | Distilled. | as $Zn_2P_2O_7$. | as $BaSO_4$. |
| Upper layer | 1·333 | 1·357 | 0·2146 | 0·2137 |
| Lower layer | 1·537 | 1·551 | 2·452 | 2·445 |
| Wet solid | 0·5933 | 0·5992 | 1·153 | 1·142 |

The correspondence of these results shows that the solid formed is not basic, and that in each layer zinc is only present as normal sulphate and ammonia only in the free state.

FIG. 1.

*Isothermal for the system* $ZnSO_4$–$NH_3$–$H_2O$ *at* 0°.

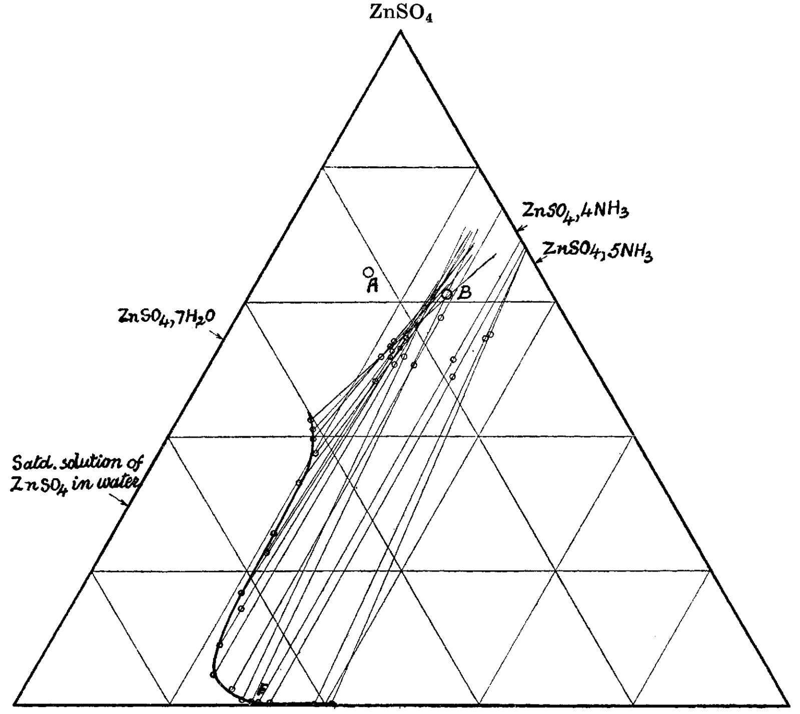


TABLE I.

*Data at* 0°.

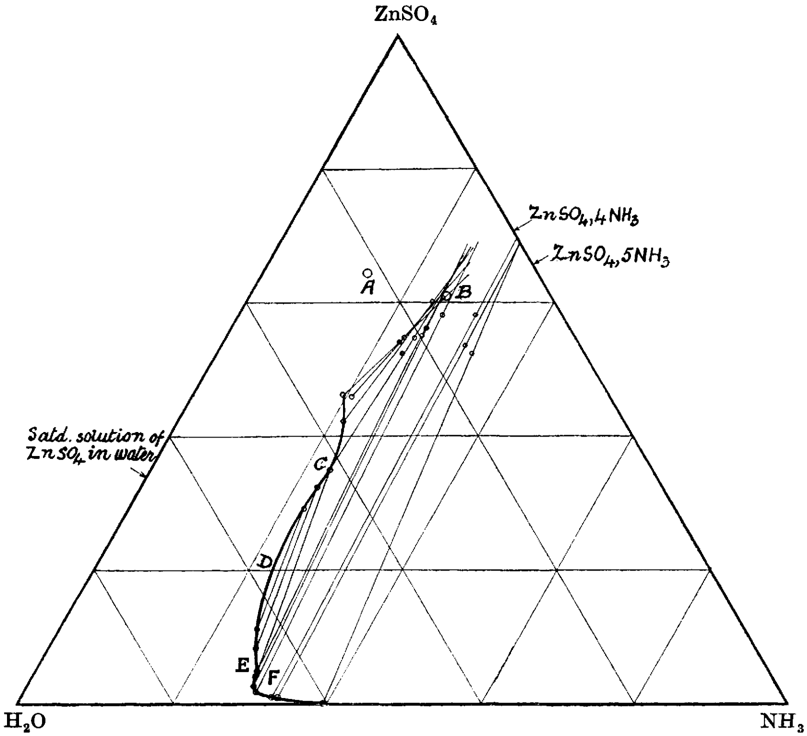
| Solution. | | | Wet solid. | | |
|---|---|---|---|---|---|
| *d.* | $NH_3$. | $ZnSO_4$. | $NH_3$. | $ZnSO_4$. | |
| 1·435 | 17·75 | 42·20 | 21·75 | 51·50 | A |
| 1·411 | 18·21 | 40·98 | 22·23 | 53·98 | |
| 1·380 | 18·87 | 39·65 | 22·36 | 53·34 | |
| 1·292 | 20·20 | 37·44 | 22·81 | 52·41 | |
| 1·180 | 20·83 | 25·83 | — | — | |
| 1·147 | 21·30 | 22·52 | 23·08 | 51·85 | |
| 1·097 | 21·26 | 16·14 | 23·57 | 54·83 | |
| 1·057 | 22·05 | 14·33 | 23·46 | 53·16 | |
| 1·006 | 21·89 | 8·98 | 23·32 | 53·23 | |
| 0·956 | 23·56 | 4·37 | 23·75 | 50·74 | A |
| 0·917 | 26·79 | 1·26 | 26·76 | 57·82 | |
| 0·912 | 29·30 | 0·65 | 24·86 | 51·75 | |
| 0·903 | 30·46 | 0·40 | 26·48 | 50·66 | |
| 0·900 | 31·23 | 0·35 | 31·19 | 51·45 | B |
| 0·896 | 32·86 | 0·15 | 32·50 | 48·90 | |
| — | 38·52 | trace | 33·72 | 54·23 | |
| — | 38·41 | ,, | 33·31 | 55·94 | |
| — | 40·52 | ,, | 33·96 | 55·00 | |

Solid phase corresponding to solutions marked A = $ZnSO_4,4NH_3,2H_2O$.
,, ,, ,, ,, ,, ,, B = Solid solutions of $ZnSO_4,4NH_3$ and $ZnSO_4,5NH_3$.

The experimental results are given in Tables I and II and are represented in Figs. 1 and 2. Concentrations are expressed as g. per 100 g. of solution.

FIG. 2.

*Isothermal for the system* $ZnSO_4$-$NH_3$-$H_2O$ *at* 18°.



## TABLE II.

*Data at* 18°.

| Lower layer. | | | Upper layer. | | | Solid. | | |
|---|---|---|---|---|---|---|---|---|
| *d.* | $NH_3$. | $ZnSO_4$. | *d.* | $NH_3$. | $ZnSO_4$. | $NH_3$. | $ZnSO_4$. | Phases. |
| 1·488 | 19·24 | 46·22 | — | — | — | — | — | $ZnSO_4,4NH_3,2H_2O$, solution, vapour. |
| 1·477 | 19·48 | 46·47 | — | — | — | 22·73 | 56·15 | |
| 1·457 | 20·37 | 46·02 | — | — | — | 23·07 | 57·09 | |
| 1·395 | 21·70 | 42·13 | — | — | — | 24·18 | 60·14 | |
| 1·304 | 23·32 | 36·97 | 0·928 | 28·74 | 4·44 | — | — | $ZnSO_4,4NH_3,2H_2O$, two solutions, vapour. |
| 1·233 | 23·07 | 32·20 | 0·967 | 26·34 | 7·82 | — | — | Two solutions, vapour. |
| 1·201 | 22·85 | 29·38 | 0·995 | 25·30 | 10·71 | — | — | |
| — | — | — | 0·929 | 28·68 | 4·01 | 24·66 | 56·35 | $ZnSO_4,4NH_3,2H_2O$, solution, vapour. |
| — | — | — | 0·911 | 29·07 | 2·20 | 25·59 | 54·76 | |
| — | — | — | 0·895 | 30·03 | 1·23 | 26·46 | 57·96 | |
| — | — | — | 0·887 | 32·43 | 0·43 | 31·55 | 57·96 | Solid solutions of $ZnSO_4,4NH_3$ and $ZnSO_4,5NH_3$, solution, vapour. |
| — | — | — | 0·880 | 33·30 | 0·49 | 31·81 | 53·64 | |
| — | — | — | — | 38·75 | 0·01 | 33·60 | 52·48 | |

## *Discussion of Results.*

The solubility curves given in Figs. 1 and 2 are not extended to the $ZnSO_4$–$H_2O$ side of the triangle. This is due to the separation of zinc hydroxide or basic salt at small concentrations of ammonia. It is only after these have been taken into solution by excess of ammonia that the solubility curve can be investigated.

The system at 18° shows the separation of two liquid layers (curve CDE) which in accordance with André's observations differ only slightly in ammonia content but markedly in their content of zinc sulphate.

At 0° there is no longer any separation of liquid phases, though the curiously distorted solubility curve of the solid (especially when considered in relation to the solubility point for zinc sulphate in water) shows that the conditions are not far removed from the possibility of liquid separation (compare Sidgwick and Ewbank's observations on salicylic acid; J., 1921, **119**, 979). Liquid layers were in fact obtained in one experiment at this temperature under conditions of slight supersaturation.

Further experiments to define more closely the conditions of liquid phase separation were performed by analysing the liquid phases saturated with solid at a series of temperatures, with the following results.

| | Lower layer. | | Upper layer. | |
|---|---|---|---|---|
| Temp. | $NH_3$. | $ZnSO_4$. | $NH_3$. | $ZnSO_4$. |
| 40° | 24·33 | 40·43 | 30·19 | 4·51 |
| 35 | 24·41 | 38·92 | 28·76 | 4·85 |
| 30 | 24·13 | 37·15 | 29·89 | 4·48 |
| 25 | 23·45 | 37·55 | 29·03 | 4·41 |
| 18° | 23·32 | 36·97 | 28·74 | 4·44 |
| 5 | — | 34·49 | — | 6·49 |
| 3 | — | 32·34 | — | 7·90 |
| 2 | — | 31·46 | — | 8·28 |

The layers are thus still very different in composition at 2°. It is concluded that the lower critical solution temperature is very near 0°, certainly below 0·5°.

As in the previous communication, an attempt was made to reach the upper critical solution temperature by heating the four-phase system, but here again a temperature of 175° was reached without any sign of coalescence.

Two different solid phases enter into the system both at 0° and at 18°. Below about 30% of ammonia the solutions are in equilibrium with an ammine hydrate, whose composition is shown fairly clearly by the tie-lines to be $ZnSO_4,4NH_3,2H_2O$ a compound previously prepared by Kane (*Ann. Chim. Phys.*, 1839, **72**, 304) by efflorescence of the corresponding tetrahydrate, and also by Müller (*Annalen*, 1869, **152**, 213) by precipitation by means of alcohol from an ammoniacal solution of zinc sulphate. The composition given by André for the solid phase, *viz.*, $ZnSO_4,2NH_3,3H_2O$, is certainly incorrect, as the phase-rule diagrams show.* The tetrammine dihydrate is deliquescent and has a high ammonia dissociation pressure, and the specimen examined by André no doubt changed in composition during its preparation for analysis.

At both temperatures when the concentration of ammonia exceeds 30% (points F) the tie-lines no longer converge to the ammine hydrate but strike the side of the triangle between the points representing the anhydrous ammines $ZnSO_4,5NH_3$ and $ZnSO_4,4NH_3$. These ammines have been shown by Ephraim (*Ber.*, 1919, **52**, 957) to form solid solutions, and there is little doubt that such solid solutions constitute the solid phases in the system now described. It was noticeable that the change from the region of tetrammine dihydrate to that of solid solutions was accompanied not only by a change in the appearance of the solid phase but also by a marked increase in the sluggishness with which the systems came into equilibrium.

## *Summary.*

(1) The system zinc sulphate–ammonia–water has been investigated at 0° and 18°.

(2) Separation of two liquid layers takes place above a lower critical solution temperature, which is approximately 0·5°. When saturated with salt, the layers persist to temperatures exceeding 175°.

(3) The solid phases formed by the system at 0° and 18° are the tetrammine dihydrate $ZnSO_4,4NH_3,2H_2O$ and solid solutions of the anhydrous pentammine and tetrammine.

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